Efficient production of the liquid fuel 2,5-dimethylfuran from 5-hydroxymethylfurfural over Ru/Co$_3$O$_4$ catalyst

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ABSTRACT

Ru/Co$_3$O$_4$ catalyst prepared by a simple coprecipitation method, was used to catalyze the conversion of 5-hydroxymethylfurfural (HMF) into 2,5-dimethylfuran (DMF) for the first time and exhibited excellent catalytic performance. 93.4% yield of DMF was achieved at relatively low reaction temperature and H$_2$ pressure (130 °C, 0.7 MPa). Further studies showed that Ru is responsible for hydrogenation, while CoO$_x$ species played important role in the hydrogenolysis of hydroxyl groups. Besides, this catalyst also displayed a good reusability and can be used for 5 times without loss of the activity.

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1. Introduction

At present, fossil fuels such as petroleum, coal, and natural gas play dominant roles as sources for energy and chemicals. However, these nonrenewable resources have come to a period of depleting reserves, which indicate the sustainable sources of energy are needed in the near future [1,2]. Biofuels that are obtainable from renewable sources have attracted recent interest [3–5]. The ultimate goal of current research is to transfer abundant renewable biomass resources to liquid fuels suitable for the transportation sector thus diminishing our reliance on petroleum [6–9].

The platform molecular, 5-hydroxymethylfurfural (HMF), a hexose dehydration product, will be a key player in the biobased renaissance because it can be converted into γ-valerolactone, levulinic acid, ethyl levulinate, as well as the promising fuel 2,5-dimethylfuran (DMF) [10–14]. DMF is particularly attractive because of its nearly ideal boiling point (92–94 °C), its high energy density (30 kJ cm^{-3}), and its high research octane number (RON = 119). Furthermore it is immiscible with water and is easier to blend with gasoline than ethanol.

CuRu/C and Pd/C catalysts are most commonly used in the conversion of HMF to DMF by hydrogenolysis. Román-Leshkov et al. [10] developed a catalytic strategy for the production of DMF from fructose. Firstly, they prepared HMF in high yields by the acid-catalyzed dehydration of fructose in a biphasic reactor, and then HMF was converted to DMF over CuRu/C catalyst. However, the catalyst is slowly deactivated and needs to be regenerated. In addition, the CuRu/C catalyst is affected to some extent by the presence of chloride ions. Thananatthanachon and Rauchfuss [15] provided a milder pathway for the production of DMF using formic acid as a reagent and Pd/C as catalyst. Heating a solution of HMF in refluxing THF with formic acid, H$_2$SO$_4$, and Pd/C gave DMF. The reaction proceeded in excellent yield. However, for the high yield, formic acid and H$_2$SO$_4$ must be used. Formic acid and H$_2$SO$_4$ are highly corrosive and is very harmful to humans and environment, and so makes this reaction process less eco-friendly.

Herein, Ru/Co$_3$O$_4$ catalyst, which was easily prepared by coprecipitation method, was used in the conversion of HMF to DMF. The Ru/Co$_3$O$_4$ catalyst showed high activity and selectivity, as well as good recyclability in the conversion of HMF to DMF. We also investigated that how the performance of the catalyst was influenced by changing the reaction temperature, pressure, the loading of Ru, HMF concentration and the support. The stability of the catalyst was also investigated.

2. Experimental

2.1. Materials

5-Hydroxymethylfurfural (99.0%) was purchased from Shanghai De-Mo Pharmaceutical Science and Technology Limited Company

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(China). 2,5-Dimethylfuran (99.0%) and $RuCl_3 \cdot 3H_2O$ were purchased from Aladdin Reagent Limited Company. $Co(NO_3)_2 \cdot 6H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tetrahydrofuran (THF) was purchased from Shanghai Chemicals Company.

2.2. Catalyst preparation

The Ru/Co_3O_4 precursor was prepared by co-precipitation method. Solution A, containing 0.045 mol $Co(NO_3)_2 \cdot 6H_2O$ and 0.001 mol $RuCl_3 \cdot 3H_2O$ with a mass composition of Ru/Co = 5 wt.%, and solution B, containing 0.13 mol NaOH and 0.065 mol Na_2CO_3 were added dropwise into deionized water at room temperature under vigorous stirring to maintain the pH value between 10.7 and 11.2. Then the mixture was heated to 80 °C for 24 h under magnetic stirring. After cooling down to room temperature, the solid precipitate was collected by centrifugation and washed with deionized water until the pH of the filtrate was ca. 7. The resulting Ru/Co_3O_4 precursor was obtained after drying at 100 °C in air for 12 h. The as-prepared precursor was calcined at 500 °C for 4 h with a ramp of 2 °C min^{-1} in air to get the corresponded RuO_x/Co_3O_4. Then the obtained material was reduced at 200 °C with flowing H_2 in tube furnace for 2 h with a ramp of 2 °C min^{-1} before used as a catalyst, N_2 was used to protect the final black powder from atmosphere. The final Ru loading in the calcined catalysts determined by inductively coupled plasma (ICP-AES) were 3.2 wt.%, approximately agreement with the initial Ru content.

For other Ru/Co_3O_4 catalyst with different loading of Ru, calculated amount of $RuCl_3 \cdot 3H_2O$ was added, other procedures were the same as above.

2.3. Characterizations of the catalyst

X-ray diffraction patterns (XRD) were recorded with a Rigaku D/max-2550VB/PC diffractometer using Cu Kα radiation. Transmission electron microscope (TEM) image was carried out with TECNAI 20S-TWIN. Chemical analyses of the samples were performed by using inductively coupled plasma atomic emission spectrometry (ICP-AES). The temperature-programmed reduction (H_2-TPR) experiment was carried out in a gas mixture of 5 vol.% hydrogen in nitrogen at a flow rate of 30 cm^3 min^{-1} and a heating rate of 10 °C min^{-1} from 25 to 800 °C. H_2 uptake was measured using a TCD detector.

2.4. Catalytic activity tests

Reactions were carried out in a stainless steel autoclave (50 mL) heated in a temperature-controlled furnace. The mixture of HMF (0.25 g), THF (10 mL), tridecane (0.25 mL, internal standard) and catalyst (0.1 g) were put in the sealed autoclave equipped with a magnetic stirring bar. The system was pressurized with H_2 before heating. After reaction, the reactor was cooled to room temperature by loading cooling water. The solid catalyst was removed by filtration, and the filtrate was taken for analysis by using a Perkin–Elmer Clarus 500 gas chromatography with a SE-54 column. The recovered catalyst was washed with THF, then dried at 100 °C for the next run. The conversion and selectivity were based on the internal standard method. The structural characteristics of the products were further identified by GC-MS.

3. Results and discussion

3.1. Conversion of HMF to DMF

At 130 °C, 0.7 MPa, the conversion of HMF was higher than 99.0% and the yield of DMF was reached 93.4%, this is a high

Table 1
Results of the conversion of HMF over various heterogeneous catalysts.[a]

Entry	Catalysts	T (°C)	P (MPa)	Conv. (%)	Y_{DMF} (%)
1	Ru/Co_3O_4	130	0.7	>99	93.4
2	Ru/Co_3O_4[b]	150	1.0	>99	75.1
3	Ru/Al_2O_3	130	0.7	>99	7.0
4	Ru/ZSM-5	130	0.7	>99	5.4
5	Co_3O_4	130	0.7	54.9	3.2

[a] Reaction conditions: catalyst, 0.1 g; HMF, 0.25 g; THF, 10 mL; reaction time, 24 h.
[b] HMF was produced from fructose in a biphase.

value under mild condition. In order to investigate the functions of Ru and Co on the conversion of HMF, the controlled catalysts, Ru/Al_2O_3 and Ru/ZSM-5 were tested and the catalytic performance is summarized in Table 1. It can be seen that both Ru/Al_2O_3 and Ru/ZSM-5 have poor selectivity to DMF. Their main product is bis(hydroxymethyl)furan (BHMF) (HMF conversion >99%), meaning that these two catalysts have an excellent activity towards hydrogenation (from carbonyl group to hydroxyl group), but they have not the ability to cleavage C—O band (hydrogenolysis). When Co_3O_4 was used as catalyst, a low HMF conversion and a poor DMF yield were obtained, meaning that the hydrogenation activity of Co_3O_4 is low. Xu et al. [16] have reported that the early transition metal oxides, for example, CoO_x could effectively break the C—O bond. So, when Ru/Al_2O_3 and Ru/ZSM-5 were used as catalysts, the main product is BHMF. When the hydrogenation activity of the metal is lower, the conversion of HMF would be low (like Co_3O_4 catalyst).

The reaction pathways are investigated by following the experiment at different reaction times. The time course of the conversion of HMF catalyzed by 5 wt.% Ru/Co_3O_4 is shown in Fig. 1 and the proposed pathways are drawn in Scheme 1. It can be seen that the hydrogenation of C=O plays dominant role and the intermediate I (bis(hydroxymethyl)furan) is obtained in the first 3 hours. Then, product I undergoes hydrogenolysis and products II, III (2-hydroxymethyl-5-methylfuran, 2,5-dimethylfuran) are generated. Only a small amount of HMF undergoes hydrogenolysis first, then product IV (5-methylfurfural) has been hydrogenated to II. It is also noted that the formation of small amounts of V (5,5′-(oxybis(methylene))bis(2-methylfuran)), this product is formed through the dehydration of II.

3.2. Determination of the suitable conditions for the conversion of HMF to DMF

#### 3.2.1. Effects of reaction temperature and pressure
The influence of temperature and pressure in the catalytic conversion of HMF over Ru/Co_3O_4 catalyst were investigated and are summarized in Table 2. The conversions of HMF are >99% in all conditions. With the increase of reaction temperature, the yield of DMF increased slightly (Table 2, entries 1 to 4), 93.4% yield of DMF was obtained at 130 °C. At lower pressure (0.5 MPa), the intermediate products were bis(hydroxymethyl)furan (BHMF)

Table 2
The effects of temperature and pressure on the conversion of HMF over 5 wt.% Ru/Co_3O_4 catalysts.

Entry	T (°C)	P (MPa)	Conv. (%)	Y_I (%)	Y_{II} (%)	Y_{III} (%)
1	110	0.7	>99	0	7.2	86.3
2	120	0.7	>99	0	4.3	89.1
3	130	0.7	>99	0	0	93.4
4	140	0.7	>99	0	0	92.8
5	130	0.5	>99	3.4	11.2	78.6
6	130	1.0	>99	0	0	94.7
7	130	1.5	>99	0	0	85.5

Reaction conditions: catalyst, 0.1 g; HMF, 0.25 g; THF, 10 mL; reaction time, 24 h.
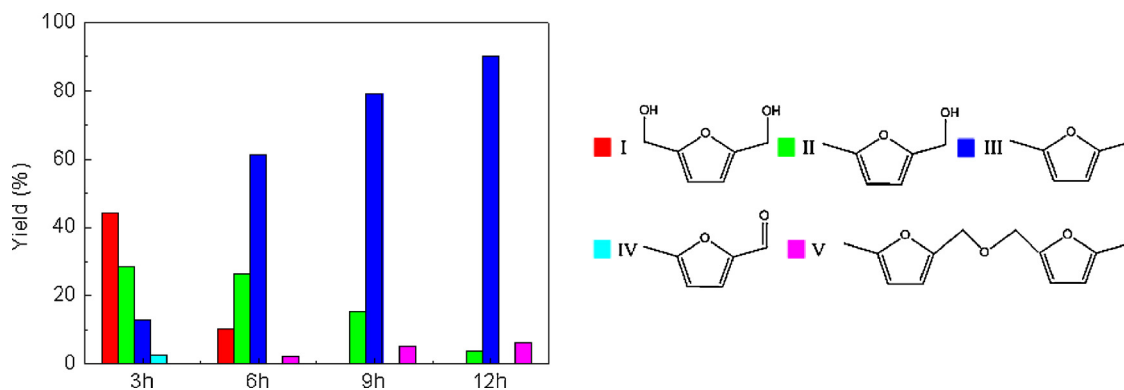
Fig. 1. Chart of yield to products in the conversion of HMF over 5 wt.% Ru/Co$_3$O$_4$ catalyst versus reaction time. (Reaction conditions: catalyst, 0.1 g; Ru/Co, 5 wt.%; HMF 0.25 g; THF, 10 mL; reaction temperature, 130 °C; H$_2$ pressure, 0.7 MPa.).
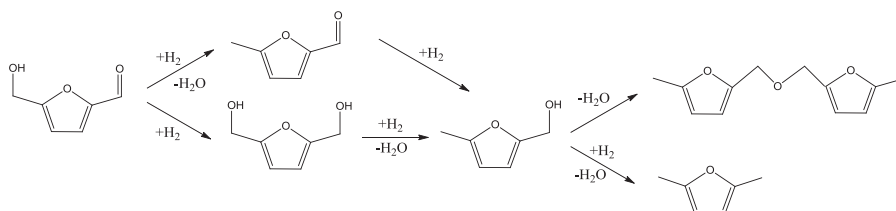
Scheme 1. The reaction pathways for the conversion of HMF.

Table 3
Effects of Ru loading and HMF concentration on the conversion of HMF over Ru/Co$_3$O$_4$ catalyst.[a]

Entry	Ru/Co (w/w) (%)	HMF/THF (w/w) (%)	Conv. (%)	Y_I (%)	Y_{II} (%)	Y_{III} (%)
1	1	2.8	85.4	15.6	37.2	27.5
2	3	2.8	>99	11.2	36.7	45.8
3	5	2.8	>99	0	0	93.4
4	7	2.8	>99	0	0	94.1
5	5	5.0	97.4	5.3	17.8	68.4
6	5	7.0	94.2	15.4	39.1	33.5
7[b]	5	5.0	>99	0	6.5	86.7

[a] Reaction conditions: catalyst, 0.1 g; THF, 10 mL; reaction temperature, 130 °C; H$_2$ pressure, 0.7 MPa; reaction time, 24 h.
[b] Charged with H$_2$ to the system for two times during the reaction.

and 2-hydroxymethyl-5-methylfuran (HMMF), meaning the hydrogenolysis was incomplete, therefore, the yield of DMF was relatively low. Further increase the reaction pressure to 1.0 MPa, the activity of the Ru/Co$_3$O$_4$ catalyst increased and a higher DMF yield was obtained. When the reaction pressure increased to

1.5 MPa, ring open and ring hydrogenation reaction happened, the yield of DMF decreased.

3.2.2. Effect of Ru loading and HMF concentration

To determine the optimum amount of Ru loading in the catalyst, a series of Ru/Co$_3$O$_4$ catalysts with different amount of Ru were prepared and tested for the conversion of HMF (Table 3, entries 1 to 4). As shown in Table 3, the yield of DMF increased notably when the amount of Ru increases from 1 to 5 wt.%. But the change was not obvious after further increase to 7 wt.%. From the view of economy and efficiency, the 5 wt.% Ru was chosen. The effect of initial HMF concentrations including 2.8 wt.%, 5 wt.% and 7 wt.% on the conversion of HMF was investigated (Table 3, entries 3, 5 and 6). It can be seen that the HMF conversion and DMF yield were affected by the initial concentration of HMF. In order to understand the decrease of the selectivity to DMF, an extra experiment (Table 3, entry 7) was carried out with charged H$_2$ to the system for two times
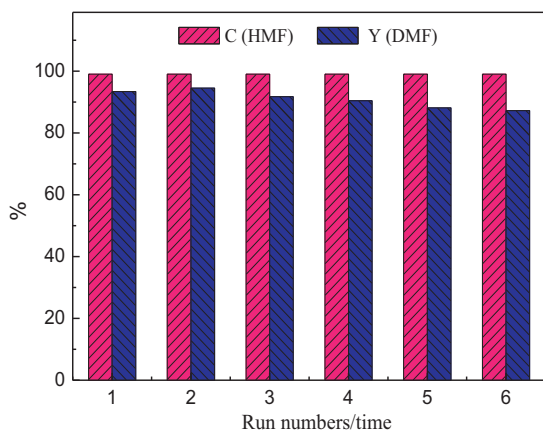
Fig. 2. The recyclability experiments of Ru/Co$_3$O$_4$ catalyst in the conversion of HMF. (Reaction conditions: catalyst, 0.1 g; HMF, 0.25 g; THF, 10 mL; reaction temperature, 130 °C; H$_2$ pressure, 0.7 MPa; reaction time, 24 h.).
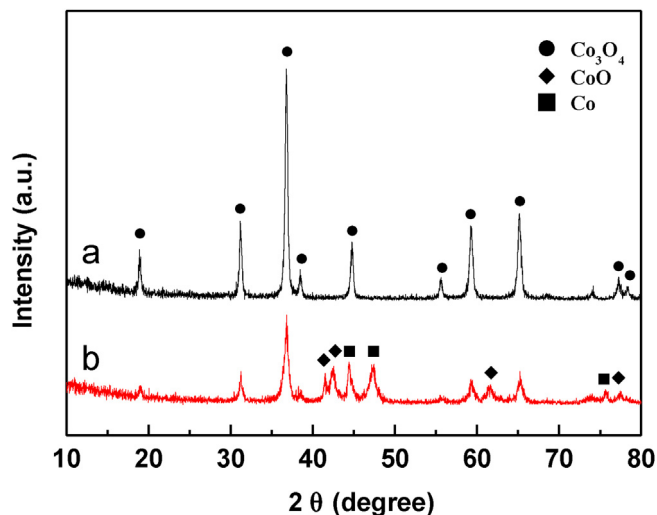
Fig. 3. XRD patterns of 5 wt.% Ru/Co$_3$O$_4$ after calcination (a) and reduction (b).
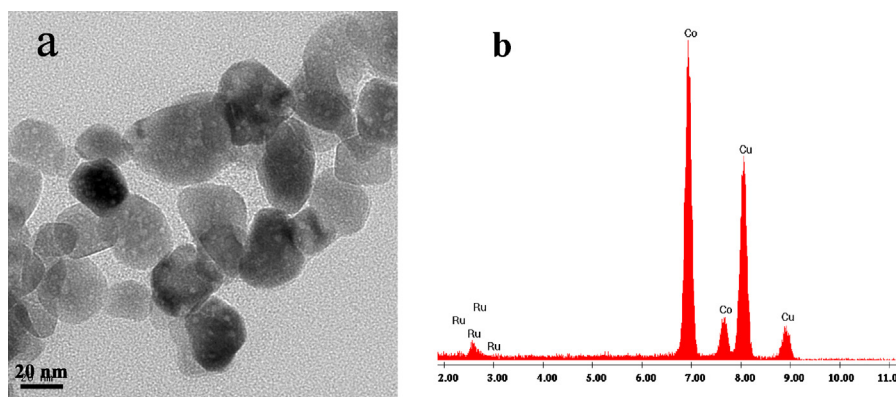
Fig. 4. TEM image (a) and EDS analysis (b) of Ru/Co$_3$O$_4$ catalyst.

during the reaction. In this case, the yield of DMF increased to 86.7%, indicating the loss of DMF yield (Table 3, entry 5) was mainly due to the lack of H$_2$. It is also indicating the high efficiency of Ru/Co$_3$O$_4$ catalyst.

3.3. Catalyst recyclability

The recyclability is of great importance for applying a catalyst in industrial processes. The recyclability of the 5 wt.% Ru/Co$_3$O$_4$ catalyst was evaluated through six repeated reactions and the results are shown in Fig. 2. It shows that the catalytic performance of the Ru/Co$_3$O$_4$ catalyst remains almost the same after being used six times, indicating the good stability of the catalyst.

3.4. Characterization of catalyst

Fig. 3 shows the XRD patterns of 5 wt.% Ru/Co$_3$O$_4$ catalysts after calcination and reduction. It can be seen from Fig. 3a that all the reflections belong to the diffraction of Co$_3$O$_4$ [17]. There are no reflections corresponding to ruthenium oxide, indicating that ruthenium oxide is highly dispersed in the sample. After reducing with H$_2$, the intensity of Co$_3$O$_4$ diffraction peaks decrease, and the reflections of CoO and Co appear, meaning that the CoO or Co^0 may be the active site beside Ru species. Considering pure Co$_3$O$_4$, after reduction at 400 °C, the activity was really increased. The conversion of HMF reached >99% with the selectivity to DMF of 38.6%, which also confirmed the activity of CoO or Co^0. The TEM images of Ru/Co$_3$O$_4$ catalyst is shown in Fig. 4. It can be seen that the nanoscaled platelets were formed in the sample. The diameters of the particles are all in the range of 20–40 nm. Although RuO$_x$ particles cannot be observed in the TEM images, the EDS analysis shows that the Ru/Co$_3$O$_4$ catalyst contains elements of Co, O and Ru, which indicates that the RuO$_x$ are highly dispersed on the support. ICP analysis showed that the Ru loading in the calcined catalyst was 3.2 wt.%, in accordance with the initial ruthenium content 5 wt.%.

The H$_2$-TPR profile (Fig. 5) of Co$_3$O$_4$ shows a main reduction peak at the range of 330–450 °C with a shoulder peak at 323 °C. According to the literature [18–20], the first peak is due to the reduction of Co$_3$O$_4$ to CoO, and the second peak is due to the reduction of CoO to metallic cobalt. For the sample of 5 wt.% Ru/Co$_3$O$_4$ catalyst, the low temperature peak at 88 °C can be attributed to the reduction of RuO$_x$. According to the literature [21], we speculate that the reduction peak at around 174 °C should be the overlapping peaks which responded to the reduction of RuO$_x$ and Co$_3$O$_4$. Furthermore, the loading of Ru resulted in the shift of the reduction peaks of Co$_3$O$_4$ to low temperature (174 °C and 205–365 °C responded to the reduction of Co$_3$O$_4$ to CoO and metallic Co, respectively).
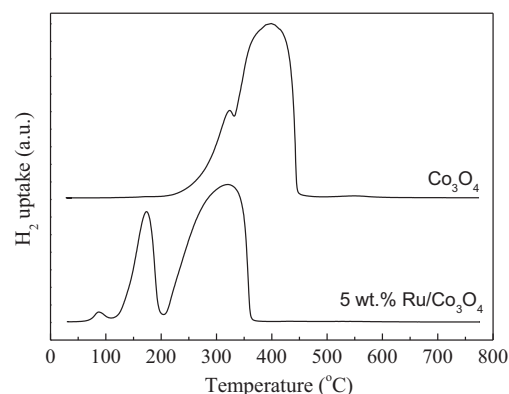

Fig. 5. Temperature programmed reduction (TPR) of Co$_3$O$_4$ and Ru/Co$_3$O$_4$ catalysts.

3.5. Extention to HMF produced from biphase (THF/H$_2$O + NaCl) reaction

We also investigated one-pot synthesis of DMF from fructose (Table 1, Entry 2): a suspension of fructose (0.5 g), NaCl (0.45 g), catalyst (sulfonated carbonaceous material, 0.25 g), THF (5 mL) and H$_2$O (1 mL) was stirred at 160 °C for 1 h. The resulting solution was then cooled to room temperature and separated into two phases, the upper layer was HMF in THF, and the lower layer was water with NaCl and some by-products. After separation, the organic phase was dehydrated by Na$_2$SO$_4$; the yield of HMF was about 81%. Then it was used in the hydrogenolysis reaction. The yield of DMF could reach 75.1%, indicating that Ru/Co$_3$O$_4$ catalyst have an excellent potential for the conversion of biomass into biofuels.

4. Conclusions

In summary, Ru/Co$_3$O$_4$ catalyst was synthesized via a simple co-precipitation method and used for the conversion of HMF to produce DMF. High activity and good reusability were obtained under mild condition; the yield of DMF can reach 93.4% at 130 °C, 0.7 MPa and can be reused for 5 times without loss of activity. This is high value under mild conditions and without noxious and corrosive materials. In this kind of catalysts, Ru is responsible for hydrogenation, while CoO$_x$ works for the absorption of hydrogenation product and then breaks the C—O bond. Ru/Co$_3$O$_4$ catalyst, due to its high activity, high reusability, has excellent potential for the conversion of biomass into biofuels.

Acknowledgements

References

[1] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angewandte Chemie International Edition 46 (2007) 7164–7183.
[2] J.B. Binder, R.T. Raines, Journal of the American Chemical Society 131 (2009) 1979–1985.
[3] G.W. Huber, S. Iborra, A. Corma, Chemical Reviews 106 (2006) 4044–4098.
[4] M. Mascal, E.B. Nikitin, Angewandte Chemie 120 (2008) 8042–8044.
[5] P. Gallezot, Green Chemistry 9 (2007) 295–302.
[6] R. Karinen, K. Vilonen, M. Niemela, ChemSusChem 4 (2011) 1002–1016.
[7] F.L. Yang, Q.S. Liu, X.F. Bai, Y.G. Du, Bioresource Technology 102 (2011) 3424–3429.
[8] P. Carniti, A. Gervasini, M. Marzo, Catalysis Communications 12 (2011) 1122–1126.
[9] Y. Roma-Leshkov, J.N. Chheda, J.A. Dumesic, Science 312 (2006) 1933–1937.
[10] Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Nature 447 (2007) 982–985.
[11] L. Deng, J. Li, D.M. Lai, Y. Fu, Q.X. Guo, Angewandte Chemie International Edition 48 (2009) 6529–6532.
[12] J.Q. Bond, D.M. Alonso, D. Wang, R.M. West, J.A. Dumesic, Science 327 (2010) 1110–1114.
[13] I.T. Horváth, J. Mehdi, V. Fábos, L. Boda, L.T. Mika, Green Chemistry 10 (2008) 238–242.
[14] J.P. Lange, W.D. van de Graaf, R.J. Haan, ChemSusChem 2 (2009) 437–441.
[15] T. Thananatthanachon, T.B. Rauchfuss, Angewandte Chemie International Edition 49 (2010) 6616–6618.
[16] W.J. Xu, H.F. Wang, X.H. Liu, J.W. Ren, Y.Q. Wang, G.Z. Lu, Chemical Communications 47 (2011) 3924–3926.
[17] L. Xue, C.B. Zhang, H. He, Y. Teraoka, Applied Catalysis B 75 (2007) 167–174.
[18] P.G. Harrison, I.K. Ball, W. Daniell, P. Lukinskas, M. Céspedes, E.E. Miró, M.A. Ulla, Chemical Engineering Journal 95 (2003) 47–55.
[19] N. Bahlawane, E.F. Rivera, K.K. Höinghaus, A. Brechling, U. Kleineberg, Applied Catalysis B 53 (2004) 245–255.
[20] H.Y. Lin, Y.W. Chen, Materials Chemistry and Physics 85 (2004) 171–175.
[21] J. Yu, D. Zhao, X.L. Xu, X. Wang, N. Zhang, Applied Catalysis B 4 (2012) 1122–1132.